Title: Review of *Sources of PCBs to the Kalamazoo River*
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The document, which was prepared by the Kalamazoo River Study Group (KRSG), was reviewed to address three questions which, along with responses, are listed below.

Question 1: *Is the information presented in the document technically correct and sufficient to support the conclusions that other sources of PCBs clearly exist other than PCBs resulting from paper recycling? If not, what are the deficiencies and what additional information would be needed.*

Response: The KRSG document claims that there is enough evidence "to prove that numerous contributors of PCBs" exist within the Kalamazoo River watershed, and "that the historical and future presence of PCBs in the watershed is not just a paper problem." The document presents some qualitative evidence supporting the possibility of sources of PCB contamination other than paper recycling, however, in most cases, the evidence cited in the KRSG document is insufficient to estimate the relative quantities of PCBs that have been released into the Kalamazoo River watershed by non-paper-recycling sources of PCBs. Quantitative information of this type is essential to making an informed decision about the relative contributions of other sources to the elevated PCB levels in fish, sediments, and water in the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site.

An analysis of the cited specific evidence (paraphrased in italics) follows.

1. *Six of 200 sites in the watershed on Michigan's Part 201 Contaminated Sites List identify PCBs as a pollutant.* The KRSG document provided no estimate of the quantities of PCBs that may be released into the Kalamazoo River from these sites relative to the quantities discharged from the sites associated with paper recycling (i.e., the King Highway Landfill-Operable Unit 3 and the Georgia-Pacific former lagoons 1, 2, 3, 4, and 5).

2. *Fourteen facilities have discharged PCBs into the Kalamazoo River.* The KRSG document provided no estimation of the relative quantities discharged from these facilities.

3. *Sixteen facilities currently have soils containing elevated levels of PCBs on site.* The KRSG document only stated that PCB soil concentrations as high as 53,000 mg/kg were detected at one location. No quantitative information was provided regarding the number of samples taken at these sites, the size of the contaminated site, the range (or mean) of PCB concentrations in the samples from each site, or the variation of the ranges (or means) across the sites. No quantitative estimates were made of the relative PCBs that may be released into the river from these sites.

4. *Eleven facilities have had documented leaks or spills of PCB-containing materials.* No documentation was provided of the quantities of PCBs leaked or spilled or the area contaminated.

5. *Thirty-five facilities purchased or used PCB-containing materials.* No estimates were provided of

the relative quantities of PCBs that were purchased and used or that may have been released from these facilities into the Kalamazoo River. Purchase and use of PCBs is not equivalent to amount released into the environment.

6. *There is clear evidence that several of the other 4 Superfund sites within the watershed have contributed substantial quantities of PCBs to the river.* The KRSG document cited qualitative evidence that 2 other Superfund sites (the Rockwell International Superfund Site in Allegan or the AutoIon Superfund Site in Kalamazoo) directly or indirectly discharged PCBs to the river in wastewater, groundwater, or surface runoff. The KRSG document only cited maximum PCB concentrations (identified to be predominately from Aroclor 1254) in samples of soils or sludge collected at the sites, PCB concentration in a single river sediment sample collected near the historical outfall from the facility on one of the sites, and anecdotal evidence of historical discharges of PCB-containing materials leaving the sites and entering the river. However, no quantitative estimates were made of the relative quantities of PCBs discharged into the river. The cited evidence is insufficient to quantitatively support the claim that these sites "contributed substantial quantities of PCBs to the river."

7. *PCBs have been discharged into the river from a number of public wastewater treatment plants within the Kalamazoo River watershed.* The KRSG document provides no information about the relative amount of PCBs discharged from these facilities compared with the amount discharged from the paper recycling sites.

8. *Upstream of the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site, elevated levels of PCBs (identified as being derived from Aroclor 1254) have been detected in fish between Battle Creek and the Morrow Lake Dam, in sediments from Morrow Lake, and in soil and sediment samples from a storm sewer ditch that historically carried discharge to the river from a Battle Creek facility. It has been estimated that 4,200 pounds of PCBs remain in Morrow Lake sediments and that 6,300 to 15,000 pounds of PCBs have historically flowed over Morrow Dam.* These data provide evidence that PCBs, have been historically discharged (predominately as Aroclor 1254) from upstream sources, and provide some quantitative estimates of the amounts that remain in, and that have been discharged downstream from, Morrow Lake. However, the KRSG document does not compare these amounts with estimates of the amounts of PCBs that remain in, or that have been discharged into the river from, the King Highway Landfill-Operable Unit 3 and the Georgia-Pacific former lagoons 1, 2, 3, 4, and 5, which are identified as principal PCB sources associated with paper recycling within the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site.

This reviewer examined one of the cited sources of the estimates of PCBs that remain in, and that have been discharged from, Morrow Lake (*PCBs in the Kalamazoo River: Update for Decision Makers. Latest Findings for Sediment, Surface Water, and Fish.* Prepared by Blasland, Bouck, & Lee, Inc. (BB&L) August 31, 2001). The BB&L document provides more complete information on the relative amounts of PCBs contributed to the river from sources upstream of the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site. This is the type of quantitative information that is not presented in the KRSG document. The BB&L document stated that approximately 1,900 kg of PCBs (4,200 pounds) are in Morrow Lake sediments (based on average PCB concentrations of 0.5 mg/kg for surficial sediments [0 to 2 inch] and 0.35 mg/kg for sediments located 2 to 6 inches below the surface) and that these concentrations were "comparable" to concentrations in samples collected within reaches of the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site proper. In addition, the BB&L document stated that approximately 2.7 kg of PCBs (about 4.8 pounds) are transported annually from upstream sources into the Site, and that this represents about 13% of the annual PCB load estimated to pass over Lake Allegan Dam at the downstream end of the Site. This estimate was based on surface water samples collected by KRSG in 2000-2001 from River Street, the sampling site located just below the Morrow Lake dam. The KRSG document does not cite this important piece of quantitative information on PCB contributions to the Site from upstream sources (i.e., 13% of annual PCB load passing over the Lake Allegan Dam).

9. *From chromatographic profiles of PCBs in carp sampled in 1993 from Bryant Mill Pond (a site expected to have been predominately contaminated with Aroclor 1242 from paper recycling), it was estimated that 84% and 16% of PCBs came from Aroclors 1242 and 1254/1260, respectively. In contrast, 100% of PCBs were estimated to be of Aroclor 1254/1260 origin in smallmouth bass and carp sampled in 1993, 1997 and 1999 from Morrow Lake (upstream of the Site), whereas smallmouth bass and carp samples collected in 1993, 1997, and 1999 from the main river channel showed average relative compositions representing 75% Aroclor 1254/1260, 22% Aroclor 1242/1248, and 3% from other Aroclors.* This information provides qualitative evidence that sources that used more highly-chlorinated PCB mixtures such as Aroclor 1254 or 1260 than the PCB mixture used in carbonless paper (Aroclor 1242) may have contributed to the PCBs found in carp and smallmouth bass sampled in the main river channel within the site, because of the apparent accumulation of more highly chlorinated PCB congeners compared with carp sampled from a pond expected to have been predominately, if not completely, contaminated with Aroclor 1242. A fairer comparison would not have averaged across carp and smallmouth bass for the main river channel, because smallmouth bass are likely to be on a higher trophic level than carp. Averaging across carp and smallmouth bass may have biased the analysis toward an Aroclor 1254/1260 determination.

Assigning an Aroclor source from the PCB congener profile in fish tissue is highly uncertain, and is more reliably made by PCB congener analysis of sediments. The uncertainty arises because PCB congeners are subject to physical weathering and biological processes that can significantly alter the composition from the original source. Enrichment of the higher-chlorinated congeners can occur in sediments due to physical weathering processes that preferentially dissolve and volatilize lower-chlorinated congeners and by preferential microbial metabolic transformations of lower-chlorinated PCBs and PCBs with chlorines in certain positions. The PCB pattern in sediments, however, are often still sufficiently similar to assign possible Aroclor sources with some reliability (Imamoglu and Christensen, 2002; Lake et al., 1995; Oliver et al., 1989). In contrast PCB profile alterations in fish tissue can become magnified with increasing trophic levels because different congeners are absorbed, metabolized, and/or eliminated to varying degrees in different organisms. Using a principal components analysis statistical technique, Schwartz et al. (1987) reported that PCB congener profiles in fish and turtle tissue were sufficiently altered to prevent the reliable identification of the original Aroclor mixture that was released into the environment.

The KRSG document provides no indication of how the total PCB concentrations in fish samples may change with increasingly downstream sample location. In contrast, the BB&L document provides such information for 1993 and 1999 samples collected from 8 locations on the river including Battle Creek and Morrow Lake (upstream of the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site), 5 locations within the Site, and Lake Allegan at the end of the Site. The data were for smallmouth bass of length less than 16 inches, and showed a general decrease (from 1993 to 1999) in total PCB concentration at all sites, and an increase in PCB concentration with increasingly downstream location, especially for the 1993 sampling period. For example in 1993, total PCB concentrations were 0.28 mg/kg wet weight in samples from Morrow Lake, 0.51 mg/kg at Mosel Avenue in Kalamazoo, 1.0 to 1.9 mg/kg at several sites between Kalamazoo and Lake Allegan, and 3.4 mg/kg at Lake Allegan at the downstream end of the Site. These data are consistent with the idea that sources within the Site discharged considerable amounts of PCBs into the river, but cannot clearly discern the relative contributions of different facilities within the site.

10. *Chromatographic profiles of PCBs in sediment samples indicated 100% Aroclor 1254/1260 in samples from Morrow Lake (collected in 2000), 98% Aroclor 1242 and 2% Aroclor 1254/1260 in samples from several "operable units" of KRSG paper residual disposal (collected in 1993/4), and 83% Aroclor 1242 and 17% Aroclor 1254/1260 in samples from the main river channel within the Site (all cores collected between 1993 and 2000).* The sediment data are consistent with the following conclusions: 1) PCB sources upstream of Morrow Lake appear to be principally associated with activities other than paper recycling; 2) KRSG paper recycling activities principally involved Aroclor 1242; 3) the predominant source of PCBs in sediments from the main river channel within the site appears to be activities associated with paper recycling; and 4) contributions to the river sediment PCB load from other PCB sources involving Aroclor 1254/1260 use is likely to be less than that from sources that used Aroclor 1242.

Question 2: *What are key EPA and peer reviewed literature which addresses PCB weathering and changes in PCB profile up the food chain?*

PCB Use: Aroclor 1242 was the only Aroclor used in carbonless copy paper in the United States.

IARC (International Agency for Research on Cancer). 1978. *Polychlorinated Biphenyls.* IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. 18: 41-103

U.S. EPA. 1976. *PCBs in the United States. Industrial Use and Environmental Distribution.* Prepared by Versar, Inc. for Environmental Protection Agency.

PCB environmental weathering: Congeners with low chlorine content tend to be more water soluble and more volatile than those with high chlorine content. Adsorption to soil and sediment tends to increase with increasing organic matter of the adsorbent and increasing chlorine content of the PCB congener. With time, these physical processes can lead to changes in PCB profiles in soils and sediments characterized by enrichment in the higher-chlorinated congeners as the lower-chlorinated congeners dissolve or volatilize.

Cogliano, V.J. 1998. Assessing the cancer risk from environmental PCBs. Environ. Health Perspect. 106 (6):317-323.

Cacela, D., Beltman, D.J., and Lipton, J. 2002. Polychlorinated biphenyl source attribution in Green Bay, Wisconsin, USA, using multivariate similarity among congener profiles in sediment samples. Environ. Toxicol. Chem. 21: 591-1599.

Erickson, M.D. 2001. Introduction: PCB Properties, Occurrence, and Regulatory History. In. *PCBs. Recent Advances in Environmental Toxicology and Health Effects.* Robertson, L.W. and Hansen, L.G., eds. pp. xi-xxx. The University Press of Kentucky.

Imamoglu, I. and Christensen, E.K.. 2002. PCB sources, transformations, and contributions in recent Fox River, Wisconsin sediments determined from receptor modeling. Water Research 36:349-3462.

Imamoglu, I., Li, K., and Christensen, E.K. 2002. PCB sources and degradation in sediments of Ashtabula River, Ohio, USA, determined from receptor modeling. Water Sci. Technol. 46:89-96.

Oliver, B.G., Charlton, M.N., and Durham, R.W. 1989. Distribution, redistribution, and geochronology of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in Lake Ontario sediments. Environ. Sci. Technol. 23:200-208.

U.S. EPA. 1979. *Water-related Environmental Fate of 129 Priority Pollutants, Vol. 1.* EPA-440-4-79-029a.

U.S. EPA. 1993. *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories. Vol 1. Fish Sampling and Analysis.* EPA 823-R-93-002.

Changes in PCB profile up the food chain: Anaerobic bacteria can reductively dechlorinate PCB congeners, with preferential removal from meta and para positions (and enrichment of ortho-substituted mono-, di-, or tri-chlorinated congeners) (Abramowicz, 1990; Alder et al., 1993; Rhee et al., 1993; Rhee and Sokol, 1994). Aerobic bacteria can dechlorinate PCB congeners with low chlorine content and oxidatively break open the phenyl rings (Abramowicz, 1990; Cogliano, 1998). In general, metabolism of PCBs in microbes and animals is slow, but PCB congeners with higher chlorine contents are more resistant to metabolism than lightly chlorinated congeners. Part of the resistance of higher-chlorinated congeners to metabolism may be related to the higher partitioning of these congeners into fatty tissue. In general, enrichment of higher-chlorinated PCB congeners in tissue occurs with increasing trophic level (Gerstenberger et al., 2000; Kim et al., 2002; Morrison et al., 1999; Niimi and Oliver, 1989; Oliver and Niimi, 1988; Lake et al., 1995). The distributions of PCBs in organisms from higher trophic levels may not closely resemble original Aroclor mixtures due to environmental, physiologic, and metabolic alterations that vary across congeners and can become more pronouncedly different with increasing trophic level (Gerstenberger et al., 2000; Kim et al. 2002; Lake et al., 1995; Schwartz et al., 1987).

Abramowicz, D.A. 1990. Aerobic and anaerobic biodegradation of PCBs: a review. Crit. Rev. Biotechnol. 10:241-245.

Alder, A.C., Haggblom, M.M., Oppenheimer, S.R., and Young, L.Y. 1993. Reductive dechlorination of polychlorinated biphenyls in anaerobic sediments. Environ. Sci. Technol. 2&:530-538

Cacela, D., Beltman, D.J., and Lipton, J. 2002. Polychlorinated biphenyl source attribution in Green Bay, Wisconsin, USA, using multivariate similarity among congener profiles in sediment samples. Environ. Toxicol. Chem. 21: 591-1599.

Cogliano, V.J. 1998. Assessing the cancer risk from environmental PCBs. Environ. Health Perspect. 106 (6):317-323.

Gerstenberger, S.L., Dellinger, J.A., and Hansen, L.G. 2000. Concentrations and frequencies of polychlorinated biphenyl congeners in a Native American population that consumes Great Lakes fish.

Clinical Toxicology 38:729-746.

Kim, S.K., Lee, D.S., and Oh, J.R. 2002. Characteristics of trophic transfer of polychlorinated biphenyls in marine organisms in Incheon North Harbor, Korea. Environ. Toxicol. Chem. 21:834-841.

Lake, J.L. McKinney, R., Lake, C.A., Osterman, F.A., and Heltshe, J. 1995. Comparison of patterns of polychlorinated biphenyl congeners in water, sediment, and indigenous organisms from New Bedford Harbor, Massachusetts. Arch. Contam. Toxicol. 29: 207-220.

Morrison, H.A., Whittle, D.M., Metcalfe, C.D., and Niimi, A.J. 1999. Application of a food web bioaccumulation model for the prediction of polychlorinated biphenyl, dioxin, and fran congener concentration in Lake Ontario aquatic biota. Can. J. Fish. Aqua. Sci. 56:1389-1400.

Niimi, A.J. and Oliver, B.G. 1989. Distribution of polychlorinated biphenyl congeners and other halocarbons in whole fish and muscle among Lake Ontario salmonids. Environ. Sci. Technol. 23:83-88.

Oliver and Niimi, 1988. Trophodynamic analysis of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in the Lake Ontario ecosystem. Environ. Sci. Tech. 22:388-397.

Rhee, G-Y., Bush, B., Bethoney, C.M., DeNucci, A., Oh, H-M., and Sokol, R.C. 1993. Reductive dechlorination of Aroclor 1242 in anaerobic sediments: pattern, rate and concentration dependence. Environ Toxicol Chem 12: 1025-1032.

Rhee, G-Y. And Sokol, R.C. 1994. The fate of polychlorinated biphenyls in aquatic sediments. Gt. Lakes Res. Rev. 1:23-28

Schwartz, T.R., Stalling, D.L., and Rice, C.L. 1987. Are polychlorinated biphenyl residues adequately described by Aroclor mixture equivalents? Isomer-specific principal components analysis of such residues in fish and turtles. Environ. Sci. Technol. 21:72-76.

Trowbridge A.G. and Swackhamer, D.L. 2002. Preferential biomagnification of aryl hydrocarbon hydroylase inducing polychlorinated biphenyl congeners in the Lake Michigan, USA, lower food web. Environ. Toxicol. Chem. 21:334-341.

U.S. EPA. 1979. *Water-related Environmental Fate of 129 Priority Pollutants, Vol. 1.* EPA-440-4-79-029a.

Question 3: *What reasons could explain differences in PCB profiles found in sediments and fish?*

As discussed in response to evidence item 9 under question 1, PCB profiles in sediments are expected to change less over time (i.e., remain more like the original Aroclor profile) than PCB profiles in fish. This is because changes from biological processes leading to enrichment of higher chlorinated PCB congeners can become magnified across trophic levels. Thus, the greater abundance of higher-chlorinated PCB congeners in fish could be a combined result of release of higher chlorinated Aroclor mixtures (1254 or 1260) into the river and trophic magnification of biological processes that lead to enrichment of higher-chlorinated PCB congeners.